SCOPE OF WORK
Regional Applied Research Effort (RARE) Proposal

Evaluating a water treatment method to prevent the formation and export of MeHg in restored wetlands and ricelands of the Sacramento-San Joaquin Delta (Delta)

United States Environmental Protection Agency
and
United States Geological Survey

Historical Perspective and Problem Statement

Beginning in the 1850s, settlers diked and drained the vast tidal marshes of the Sacramento-San Joaquin Delta (Delta) and commenced farming practices that oxidized and destroyed peat soils. A century later, the Central Valley Project (completed in 1940) and the State Water Project (completed in 1967) were constructed in a way that relied on the original network of levees built by the settlers. However, by the year 2000, the Delta islands surrounded by the levees had subsided to between 5 and 30 feet below sea level (Ingebritsen et al. 2000; Miller et al., 2011; Figure 1). This land subsidence has made the levees vulnerable to collapse, and has placed at risk the centerpiece of California's water supply system. A collapse of the levees caused by an earthquake, a storm, or ongoing sea level rise would allow salt water to intrude into the Delta from San Francisco Bay, and would result in the replacement of low-lying farmlands with permanent open water features (Drexler et al., 2009).

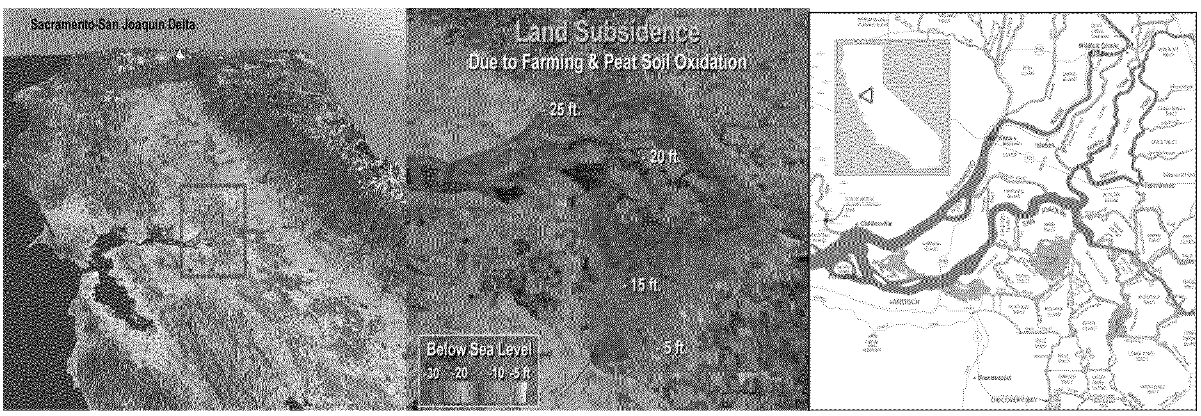

Figure 1. Land subsidence in the Sacramento-San Joaquin Delta

Today, agencies and non-governmental organizations (NGOs) are proposing to restore tens of thousands of acres of wetlands across the Delta. Restoring wetlands on deeply subsided islands within the Delta would provide an array of benefits including the reversal of land subsidence, stabilization of levees, protection of water supply infrastructure, expansion of estuarine habitat, and mitigation of climate change through the capture and storage of atmospheric carbon. However, anaerobic conditions within wetlands can transform mercury (Hg) present in the soils into monomethyl mercury (known more commonly as methyl mercury or MeHg). Sources of the mercury include historic inputs from the Gold Rush era; drainage from abandoned mines in the Coast Range, Diablo Range, and Sierra Nevada; and ongoing air deposition from domestic industry and international coal-fired power plants.

Mercury is a neurotoxin that can bioaccumulate in organisms to levels that adversely affect the health of fish, wildlife, and people (Selin 2009; Mergler et al., 2007). Total Hg in surface waters can be separated into two general fractions, inorganic Hg (IHg)[1] and methyl mercury (MeHg). MeHg is a the more bioavailable form of the metal, formed primarily under anaerobic conditions (Compeau and Bartha 1985; Gilmour et al 1995). When MeHg is formed by anaerobic processes in restored wetlands and farmed ricelands, it bioaccumulates in aquatic life, and enters Delta channels when water is drained or pumped from the island. Landowners and reclamation districts continually pump water from the interior of subsided islands to prevent flooding and to keep the islands available for ongoing agriculture. Wood et al. (2010) estimated that ~40% of the aqueous MeHg present in the Bay Delta Estuary may be produced *in situ* within Delta wetlands. Methods must be devised to prevent the formation and transport of MeHg to clear the way for large-scale wetlands restoration plans.

In the fall of 2011, under the Regional Applied Research Effort (RARE) program, EPA Region 9 recommended for funding a research project proposed by the USGS' California Water Science Center that will evaluate the efficacy of a water treatment method known as *Low Intensity Chemical Dosing* (LICD) in preventing the formation and transport and MeHg from wetlands and ricelands into surface waters of the Delta. Under this method, drainage water flowing from the islands into Delta channels will be treated with metal-based coagulants in an effort to precipitate out of solution dissolved organic carbon (DOC), IHg, and MeHg. The resulting metal-organic complex termed flocculent (floc) would then be sequestered within accreting layers of aquatic vegetation as wetlands are established to increase the areal extent of emergent marsh, reverse subsidence, and stabilize levees.

EPA's RARE project will build upon the research previously funded by the California Department of Water Resources[2] whereby USGS and its partners[3] constructed a replicated field experiment to examine how: (1) constructed wetlands can be reestablished on subsided islands; and (2) iron and aluminum-based coagulants can sequester DOC from island drainage prior to discharge into Delta waters. These

[1] Inorganic Hg (IHg) is calculated as total Hg in solution minus MeHg.
[2] DWR Agreement #: 4600003886
[3] Bachand and Associates; UC Davis

coagulants, routinely used to remove DOC from drinking water prior to disinfection, cause DOC to precipitate as a floc.

With funding secured from EPA's RARE program, USGS will expand the scope of its original research beyond the efficacy of LICD in sequestering DOC, and toward the efficacy of LICD in sequestering IHg and MeHg. Both IHg and MeHg are largely associated with DOC and are therefore similarly sequestered in the floc. Laboratory studies indicate that more than 90% of IHg and 70% of MeHg can be removed from the water column using the LICD treatment process (Henneberry et al., 2011).

If the efficacy of the LICD treatment method can be validated and scaled-up, then the method can be used to advance the implementation of large-scale weltands restoration projects. In turn, these projects can both provide the array of benefits referenced above, and contribute to the pollutant load reductions mandated by the State's Delta Methylmercury TMDL[4].

Expanding the Scope of Existing Research through RARE Funding

In 1998, USGS established a pilot wetlands restoration project on Twitchell Island that demonstrated the potential to improve levee stability through the construction of wetlands on deeply subsided islands in the Delta[5]. USGS tested restoration methods on the pilot wetlands and discovered that aquatic plants (cattails, *Typha spp* and tules, *Scirpus californicus*) sequestered CO_2 and accreted enough vegetative matter to increase land surface elevations by 2 to 4.5 cm/yr. This represents an accretion rate of ~40 times the natural, historic accretion rate (Miller et al., 2011).

Until recently, the investigation of the potential harm caused by wetland creation in the Delta was limited to the production of DOC, which can form harmful disinfection byproducts (DBPs) such as trihalomethanes (THMs) when water is treated for municipal use (Fleck et al., 2007; Kraus et al. 2008). However, the pilot wetlands were found to be a potential major source of DOC, DBP precursors, and MeHg to Delta waters depending on hydrological processes and management strategies (Fleck et al., 2007; Sassone et al., 2008). The production of MeHg is facilitated by sulfate- (and possibly iron) reducing bacteria that occur in suboxic sediment. The methylation process is largely controlled by the activity of those bacteria (limited by sulfate/iron and organic matter) and by the availability of inorganic Hg to these bacteria. In 2011, USGS and its partners completed construction of the experimental cells on Twitchell Island where the LICD treatment method will be tested. The research funded by DWR

[4] http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/delta_hg/
[5] The pilot wetlands are interchangeably referenced as the "Carbon Farm" or the Carbon Capture Farming Program (CCFP). http://ca.water.usgs.gov/Carbon_Farm/

enabled USGS to test the efficacy of the LICD treatment method toward sequestering DOC. The RARE funding from EPA will allow USGS to expand the scope of their LICD studies to include both IHg and MeHg. See Figure 2.

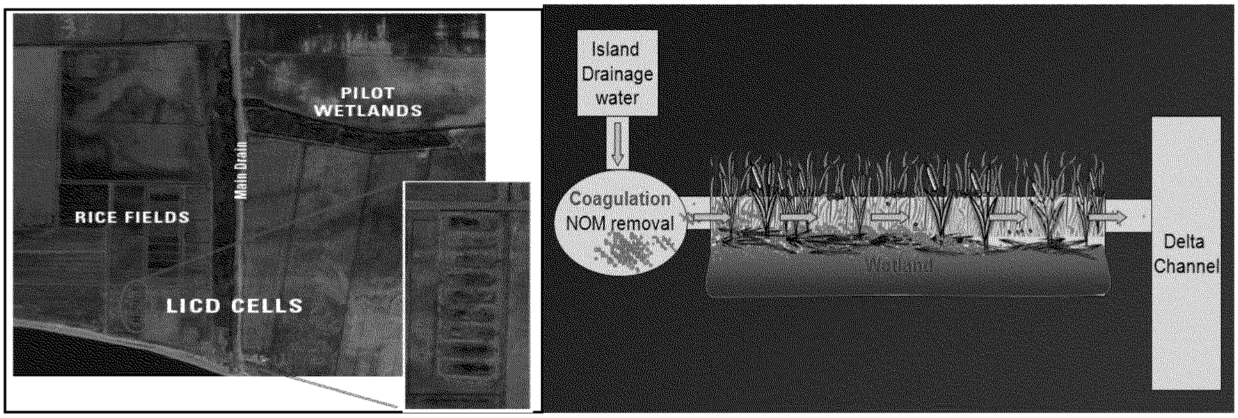

Figure 2. Pilot wetlands and LICD cells on Twitchell Island and diagram of the treatment and sequestration process.

This replicated, field-scale demonstration project comprises nine (9) wetland cells encompassing three different treatment approaches: (1) inflow water coagulated with iron sulfate (FS); (2) inflow water coagulated with polyalumnium chloride (PAC); and (3) a control cell where coagulants are not added. See Figure 3.

The metal based coagulants will bind with DOC and MeHg to form a metal-dissolved organic matter (DOM) floc which precipitates out of solution. Importantly, preliminary studies suggest that once the floc is formed, it remains stable under reducing conditions and may have the capacity to sorb additional Hg entering the wetland system (Henneberry et al., unpublished).

Settling of the floc material in constructed wetlands designed to accrete vegetative matter and rebuild peat soils could permanently trap and store carbon and mercury in successive layers of wetlands strata. The sunken Delta islands provide ~3.4 billion cubic yards of "accommodation space" wherein massive quantities of carbon and mercury could be trapped and permanently stored. In short, the LICD treatment method could turn a worrisome liability (sunken Delta islands) into a welcome asset (a permanent repository for carbon and mercury), and this would prevent these problematic elements from perpetually cycling between the media of air, land, water, and biota.

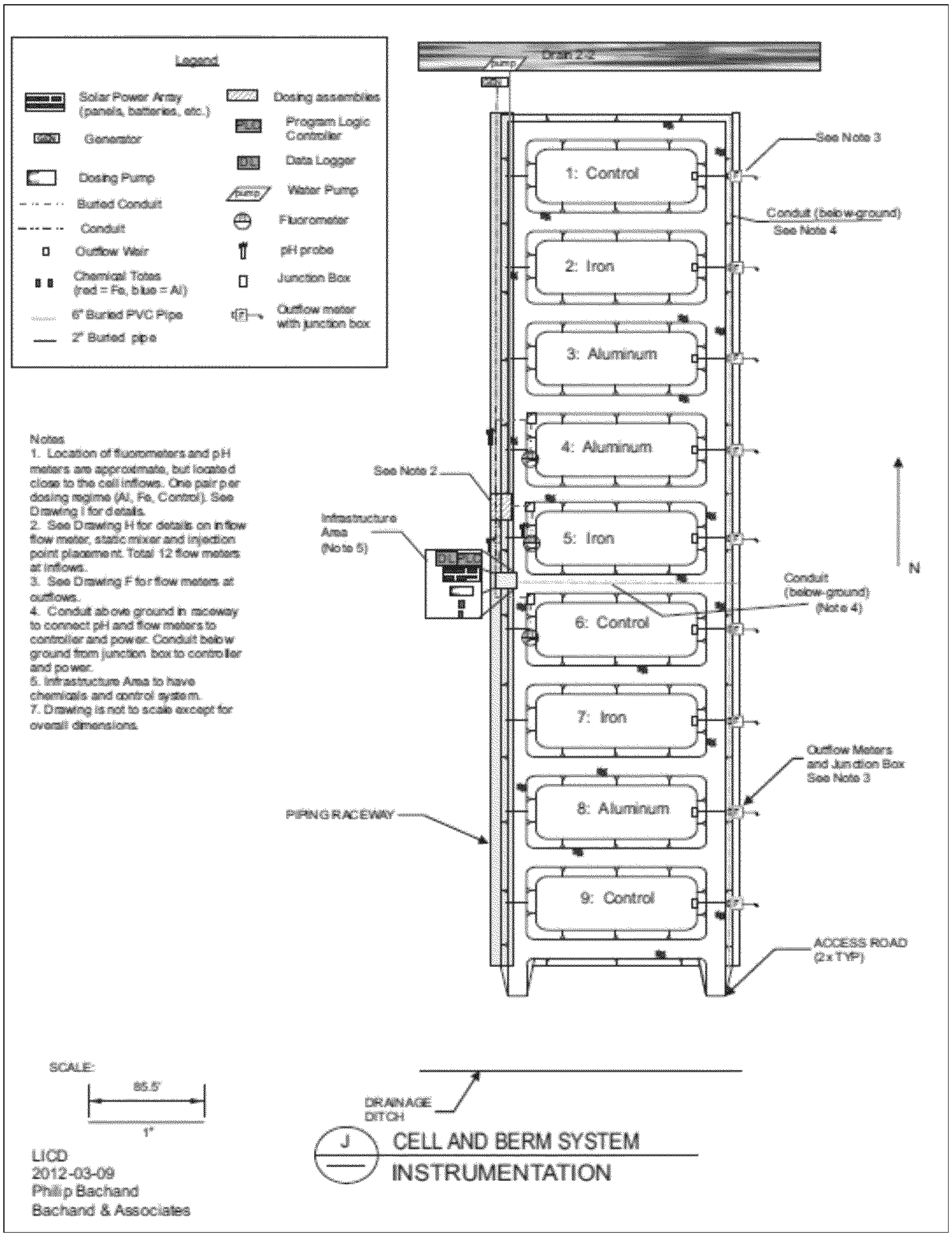

Figure 3. Schematic showing the Demonstration Wetland Study established in 2011 on Twitchell Island as part of the LICD Study.

Work Elements

1) **Quality Assurance Project Plan (QAPP):** On 23 February 2011, ORD's National Risk Management Research Laboratory (NRMRL) relayed word to EPA Region 9 that the QAPP prepared by USGS for the original LICD experiments involving DOC was acceptable for the expanded scope of the experiments under the RARE grant that will involve testing for IHg and MeHg.

2) **Sample Collection and Analysis**

   a) In conjunction with the USGS-DWR sampling schedule, surface water samples will be collected from the inflows and outflows of the nine wetland cells approximately monthly for a period of twelve (12) months. These samples will be analyzed for total and methyl mercury as part of this study. Measurement of DOC, POC (particulate organic carbon), nutrients (N, P), and metals (Fe, Al), will be conducted on sample splits as part of the USGS-DWR study. The overall framework for this LICD research is summarized in Table 1.
   b) Analysis of total and methyl Hg concentrations, in both dissolved and particulate material, will be conducted by the USGS Wisconsin Mercury Lab.
   c) Field parameters – temperature, pH, electrical conductivity, turbidity – will be measured at the time of sample collection.
   d) Statistical comparisons of the three different wetland cell treatments will be conducted to assess the effects of coagulation on (1) removal of IHg and MeHg from drainage waters prior to release into the wetland cells and (2) release of IHg and MeHg into surface waters during passage through the wetland cells.

3) **Technical Report**
   Within twelve (12) months following the completion of field work, USGS will submit to EPA a technical report that details the results of the investigation, findings, potential applications, uncertainties, and recommendations for future research.

USGS Responsibilities

USGS has the technical expertise required to perform the field sampling, chemical analysis, and data analysis. This project will use standard analytical methods acceptable to the USGS and the EPA. The USGS Wisconsin Mercury Lab (http://wi.water.usgs.gov/mercury-lab) will be used for the chemical analyses of Hg because of its ability to detect low concentrations of both total and methyl Hg. EPA's Richmond Lab does not support this type of field research and does not have the capability to analyze the samples at the detection levels required for this study.

For this IAG the USGS responsibilities include:

1) Implementation of the approved Quality Assurance Project Plan (QAPP).
2) Collection of samples and execution of chain of custody protocols in the course of submission of the samples to the Wisconsin Mercury Lab.
3) Performance of chemical analyses of water samples.
4) Compilation of analytical results in Excel workbooks.
5) Analysis of chemical data to determine the effects of LICD treatments on IHg and MeHg concentrations.
6) Collaboration on preparing any reports, journal articles, and presentations.
7) Participation in conference calls, meetings, and seminars pertaining to the research.

EPA Responsibilities

EPA will continue collaborating with USGS on all aspects of the project.

For this IAG, the USEPA responsibilities include:

1) Collaboration on data analyses and interpretation, journal articles, and presentations.
2) Participation in conference calls, meetings, and seminars pertaining to the research.
    3) Providing funding in accordance with the agreement:
    FY2012: $90,000

All project funds are to be provided through an IAG between ORD-Cincinnati and USGS' California Water Science Center.

Deliverables

Within twelve (12) months following the completion of field work, USGS will submit to EPA a technical report that details the results of the investigation, findings, potential applications, uncertainties, and recommendations for future research.

Schedule

Field work will commence once the IAG is approved and funding becomes available. Surface water samples will be collected from the inflows and outflows of the LICD cells approximately monthly for a period of twelve (12) months. Sample analysis, data compilation, and data analysis will be completed within six (6) months following the last date of sampling. See the detailed schedule in Table 2.

Budget

Personnel costs for USGS CA Water Science Center (WSC)	
Project Lead: Soil scientist (approx. 2 weeks)	$11,500
Hydrologist Mercury Specialists (approx. 3 weeks)	
@ CA Water Science Center	$10,000
@ Wisconsin Mercury Research Lab	$ 5,000
Technician (approx. 6 weeks)	$20,000
Analytical[6]	
EPA's share of analytical costs at the USGS-WMRL	$40,000
Supplies	$ 3,500
Total Cost Covered by EPA-ORD Funding	**$90,000**
In-Kind Services from USGS' Wisconsin Mercury Research Lab (WMRL)	
Consultation by WMRL's Team Leader/Project Chief	$ 5,000
USGS's share of analytical costs at the USGS-WMRL	$42,360
Total Value of In-Kind Services Rendered by USGS-WMRL	**$47,360**

Timeline

	Month																							
Task	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**
1. Sample collection and processing	x	x	x	x	x	x	x	x	x	x	x	x												
2. Analyses			x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x						
3. Data analyses and interpretation								x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
3. Report																						x	x	x

[6] Analytical costs were estimated based on the dosing set-up that delivers the same inlet water to all 3 replicated cells. The sampling design minimum is 3 inlets and 9 outlets. Samples will be collected monthly over one year.
12 samples @ 12 months +12 replicates + 12 blanks = 168 analyses for THg and MeHg, dissolved and particulate phases.
168 analyses @ $520/full analytical suite = $87,360 analytical cost on the open market.
Total value of consultation services provided by WMRL's Team Leader/Project Chief = $5,000.
Total value of services rendered by USGS' Wisconsin Mercury Research Lab = $92,360.
Total amount of EPA-ORD funding allocated to WMRL = $45,000.
Total value of in-kind services rendered by WMRL = $47,360.

Table 1. The overall framework for the LICD research.

Project Goals	Hypotheses	Approach	Expected Results	Benefits
(1) Reduce DOC and DBP precursor transport from subsided Delta islands (**DWR funding**)	H1a: LICD treatment cells will decrease DOC (and DBPP) loads relative to untreated cells (control) H1b: Iron-based coagulant will be more effective than aluminum-based coagulant	Measure DOC concentration and loads at inlets and outlets of each LICD wetland cell.	Significantly lower ($p<0.05$) DOC loads from treatment cells compared to controls. Possible differences between coagulants	Reduced drinking water contaminant (DOC) release from Delta Islands
(2) Increase accretion within wetland treatment cells (**DWR funding**)	H2: Wetlands receiving LICD floc will have greater land surface accretion and C-storage compared to untreated wetlands (control)	Measure sediment (and carbon) accreted in the wetland cells relative to land surface prior to flood-up	Significantly greater accretion and carbon storage ($p<0.05$) in treatment cells relative to control cells	Reduced hydrostatic pressure on most threatened Delta levees. Carbon sequestration ($ on C market?)
(3) Decrease IHg and MeHg loadings from subsided islands into Delta channels (**EPA funding**)	H3a: LICD treatment cells will decrease MeHg (and THg) loads relative to untreated cells (control) H3b: Iron-based coagulant will be more effective than aluminum-based coagulant	Measure THg and MeHg concentrations and loads at inlets and outlets of each wetland cell.	Significantly lower ($p<0.05$) THg and MeHg loads from treatment cells compared to controls	Demonstration of mitigation strategy to meet TMDL goals of reduced MeHg loads from high DOC systems (wetlands, agriculture)
4) Decrease Hg bioaccumulatio n in biota by sequestering material in accreting wetlands (not funded)	H4a: Biota within the wetlands receiving LICD floc will have lower THg and MeHg than control wetlands H4b: Iron-based coagulant will show greater decrease than than aluminum-based coagulant	Measure THg and MeHg concentrations in caged mosquito fish (Gambusia spp) placed in each of the LICD treatments	Significantly lower THg and MeHg concentrations or burdens ($p<0.05$) in fish collected from treatment wetlands relative to control wetlands	Demonstration of mitigation strategy to meet TMDL goals of reduced biota concentrations in Delta habitats
(5) Outreach conducted to the public by the end of the Project (**funded by DWR and EPA**)	H5: Delta communities and stakeholders will embrace alternative land use practices if feasibility and benefits are demonstrated	1) Conduct quarterly public workshops to discuss Delta issues and options. 2) Coordinate with WEF/WET to enhance discussion of Delta options (LICD, C-farming, rice production) and concerns 3) Coordinate with TMDL process to incorporate LICD into possible mitigation strategies	Demonstrate a strategy for preserving the heart of the Delta that protects its economic, ecologic and cultural identity	250-500 contacts with local landowners, Local, state and regional staff and volunteers, and other community members and stakeholders

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